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(54) Title: IMPROVEMENTS IN PRESERVATIVES FOR WOOD-BASED PRODUCTS

(57) Abstract: A method of using triadimefon and/or triadimenol as a preservative for the protection of glued wood-based products against attack and destruction of microorganisms. The method is characterized in that triadimefon and/or triadimenol is applied during the manufacturing process of the glued wood-based products.

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#### TITLE OF THE INVENTION

#### IMPROVEMENTS IN PRESERVATIVES FOR WOOD-BASED PRODUCTS

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#### FIELD OF THE INVENTION

The present invention relates to antifungal preservatives for wood-based glued products.

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#### BACKGROUND OF THE INVENTION

As a biological material, wood is subject to attack by fungiand insects. These organisms may damage the appearance of the wood, and they may seriously reduce it's structural strength. Wood and wood-based products can be protected from the effects of wood destroying organisms by applying fungicides or insecticides, or both. Such treatments can greatly improve the service life of the wood product, especially for timbers with low natural durability, such as radiata pine and other softwood species.

For some wood-based products, conventional methods of applying preservative treatment are inappropriate. For

example, water based treatments such as copper chrome arsenate ("CCA") cannot be applied to laminated veneer products, particle based products or fibre based products without causing significant degrade and product loss. Other post-manufacture treatments for these products, such as light organic solvent preservative ("LOSP") are expensive and require a further processing step to achieve the treatment, creating extra cost.

10 A method favored by some wood-based product manufacturers is the application of a preservative by addition to the glue during manufacture. This approach can be used for any wood product that is constructed from relatively thin or small particles, such as wood fibre, wood chip or flake and thin wood veneer. Plywood, laminated veneer lumber (LVL), medium density fibreboard (MDF), waferboard/strandboard/oriented strandboard (OSB) and particleboard fall into this category.

The major drawbacks with this method of application lie in the nature of the glues used in the manufacturing process and the type of compounds available for treatment.

In general, glue systems for wood based products have high pH (9-12) or are highly reactive (e.g. isocyanate based glues).

Thus the addition of a compound to such an environment can result in rapid degradation of the molecule. A further challenge to the robustness of the added compound is the curing condition for the glues. These are often high temperatures (~170°C) in a high pressure pressing system.

These conditions require that any added preservative be robust enough to retain at least some of it's activity to be effective during the service life of the product.

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It is known in the art that triazoles are generally effective against the <code>Basidiomycetes</code> , which are the fungi known to cause decay in wood. The triazoles most commonly used to protect solid wood from decay are tebuconazole and propiconazole. The amount of active ingredient needed in the wood to protect from decay has been shown to be in the order  $50g/m^3$  wood to  $300g/m^3$  wood for tebuconazole and  $220g/m^3$  wood to  $490g/m^3$  wood for propiconazole. It has also been disclosed that these two triazoles can act synergistically in some cases.

Furthermore, it is also known that due to the nature of the glue systems, the above mentioned triazoles that show activity in solid wood applications, when used in a glue-line

treatment, have to be added in large quantities to the glue mixture due to subsequent breakdown in the process or due to inhomogeneous distribution in the wood based product.

5 A need therefore continues to exist for a preservative for wood-based products that can be applied in the manufacturing of wood-based products.

Applicant has surprisingly found that triadimefon and triadimenol can be used as preservatives for the protection of wood-based products against attack and destruction of microorganisms, especially of fungi.

Surprisingly triadimefon and triadimenol are stable under the conditions of the glue-line treatment and thus can be employed as preservatives in the manufacturing of glued woodbased products. In some cases, under alkaline conditions, triadimefon is being converted into triadimenol which is stable under these conditions and which also exhibits the required biological properties.

#### OBJECTS OF THE INVENTION

It is a first object of the present invention to provide a method of using triadimefon and/or triadimenol as an antimicrobial preservative for wood-based glued products:

It is a second object of the invention to provide a composition having improved antimicrobial properties as preservative for use in the production of wood-based glued products.

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#### SUMMARY OF THE INVENTION

- According to one aspect of the present invention there is
  provided method of using triadimefon and/or triadimenol as
  a preservative for the protection of glued wood-based
  products against attack and destruction of microorganisms
  characterized in that triadimefon and/or triadimenol is
  applied during the manufacturing process of the glued
  wood-based products.
  - According to a further aspect of the invention there is provided a composition for the protection of glued woodbased products against attack and destruction of

microorganisms containing a glue, triadimefon and/or triadimenol.

## MORE DETAILED DESCRIPTION OF THE INVENTION

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(±)1-(4-chlorophenoxy)-3,3-dimethyl-1-(1H-1,2,4-triazol-1yl)butan-2-one (triadimefon) is a known triazole compound
which is used in agriculture as a fungicide, especially for
Basidiomycete control. Triadimefon has an alcohol analogue(±)

10 1-(4-chlorophenoxy)-3,3-dimethyl-1-(1H-1,2,4-triazol-1yl)butan-2-ol (triadimenol), which shows similar activity and
which is used for the same purpose. These known compounds are
being superseded in agricultural uses by newer triazole
compounds, such as propiconazole and tebuconazole, because of
their higher activity at lower use rates.

Table 1. Agriculture use rates for selected triazoles.

Active	Use rate range g/ha
	(agricultural uses) <sup>1</sup>
propiconazole	100-150
tebuconazole	100-250
triadimefon	125-500
triadimenol	125-500

<sup>1</sup> Data from The Pesticide Manual, 12<sup>th</sup> Edition. British Crop Protection Council, Farnham, Surrey, UK. 2000

When the known triazoles are applied to wood based products as for example strandboard, particleboard, Medium Density Fibreboard (MDF), Plywood and Laminated Veneer Lumber (LVL) via the glueline, the expected levels of performance are not met at a said active content as would be expected.

Surprisingly, under these conditions, triadimefon and triadimenol show remarkable and consistent efficacy at surprisingly low levels. That means, improved levels of performance relative to the low amounts of triadimefon/triadimenol added are exhibited.

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When used in the glue-line under alkaline conditions such as found in PF type glues, triadimefon may be reduced to the alcohol analogue triadimenol which surprisingly shows the same efficacy as triadimefon.

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Table 2. Effective dosing rates for tebuconazole, propiconazole and triadimefon

	<sup>2</sup> Efficacy against target organism						
¹Use rate	(expressed as weight loss per cent in a						
gram a.i./m³	standard rot trial with Tyromyces						
	palustris as the target species) 1						
	Tebuconazole	Propiconazole	Triadimefon				
80	9.2	<u> </u>	-				
100	-	20.5	3.7				
160	20.9	-	_				
200	-	7.6	0.5				
320	6.3	_	_				
400	-	21.4	0.9				
640	18.5	_	_				
800	_	1.8	1.4				
Untreated	17.5						
Commercial		5.8					
Standard							
<sup>3</sup> LOSP							

In the glueline of plywood manufactured from pinus sppusing phenol formaldehyde glue

<sup>&</sup>lt;sup>2</sup> Using Japan Wood Preservers Association Standard Test procedure

<sup>5 &</sup>lt;sup>3</sup> Light Organic Solvent Preservative (tributyl tin oxide)

The novel nature of this activity renders the triazole molecules triadimefon and triadimenol particularly suitable to the protection of glued wood based products from attack by microorganisms, especially of certain decay causing fungi.

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According to the method of the present invention triadimefon and/or triadimenol are preferably added to the glue (glue-line treatment) during the manufacturing of glued wood-based products. Surprisingly according to the present invention triadimefon and/or triadimenol can be applied at low rates while a high protection of the wood-based products is provided.

The method of the present invention preferably provides protection of the glued wood-based products against attack and destruction of fungi.

#### Examples for wood destroying fungi are:

chaetomium as chaetomium globosum or chaetomium alba-arenulum humicola grisea petriella as petriella setifera trichurus as trichurus spiralis basidiomycetes coniophora as coniophora puteana coriolus as coriolus versicolor

conkioporia as donkioporia expans glenospora as glenospora graphii gloeophyllum as gloeophyllum abietinum or gloeophyllum adoratum or 5 gloeophyllum protactum or gloeophyllum sepiarium or gloeophyllum trabeum lentinus as lentinus cyathiformes or lentinus edodes or 10 lentinus lepideus or lentinus grinus or Lentinus squarrolosus paxillus as paxillus panuoides pleurotus as pleurotus ostreatus 15 poria as poria monticola or poria placenta or poria vaillantii or poria vaporaria serpula as serpula himantoides or 20 serpula lacrymans stereum as stereum hirsutum tyromyces as tyromyces palustris.

The process of manufacturing of glued wood-based products is

25 in general commonly known. This process of manufacturing is

generally used for any wood-composite product that is

constructed from relatively thin or small particles, such as

wood fibre, wood chip or flake and thin wood veneer. Plywood,

laminated veneer lumber (LVL), medium density fibreboard

(MDF), waferboard/strandboard/oriented strandboard (OSB) and particleboard can be manufactured by that method.

During this process the thin or small wood particles are combined with each other by addition of a glue or glue system under application of pressure to form a wood composite product. It is a known practice to add a wood preservative to the glue or glue system during the manufacturing process, the so-called glue-line treatment.

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According to the method of the present invention, triadimefon and/or triadimenol are preferably added to the glue during the process of manufacturing of the wood-based products. It also possible to first prepare a composition containing a glue, triadimefon and/or triadimenol and optionally one or more solvents which are compatible with the glue or glue system and to apply such composition to the wood particles in the manufacturing process.

20 Solvents that can be used in the method of the present invention are for example N-methyl-pyrrolidone, glycolethers, texanole, benzyl alcohol, phenoxy ethanol, cyclohexanone.

High levels of glycols should be avoided because they might 25 affect the viscosity or curing times of the glues.

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Examples for the glue that can be used in the manufacturing of glued wood-based products are the following glues or glue systems: urea or urea phenol based systems as UF = urea-formaldehyde resins, PF = phenol-

5 melamine(formaldehyde)resins, MUF = melamine(formaldehyde)urea resins;

Polyvinyl alcohol (PVA) systems;

pMDI = polymeric methylene diphenyldiisocyanate.

Preferred are UF, MUF, PF and PVA systems.

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In a further embodiment of the present invention triadimefon and/or triadimenol are used in mixture with at least one further fungicide, preferably selected from tebuconazole and cyproconazole.

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It was found that surprisingly triadimefon and/or triadimenol enhance the protective effectiveness of other triazole fungicides, namely tebuconazole and cyproconazole, in glued wood based products, when applied in a combination product. Combinations of triadimefon with tebuconazole, preferably in a molar ratio of 5:1 to 1:2, or with cyproconazole, preferably in a molar ratio of 5:1 to 1:3, provide a broad protection of glued wood based products against decay causing fungi.

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In a further embodiment of the present invention triadimefon and/or triadimenol are applied in combination with one or

more insecticide that is known to be effective when applied via the glueline. Appropriate insecticides include synthetic pyrethroids - such as permethrin, cypermethrin, alphacypermethrin, deltamethrin, cyfluthrin, bifenthrin -, neonicotinoids - such as imidacloprid, clothianidin, acetamiprid, thiamethoxam -, chlorfenapyr, and fipronil. Mixtures of insecticides with triadimefon/triadimenol or combinations of triadimefon/triadimenol with tebuconazole or cyproconazole at appropriate rates will provide a simple one step application of preservative and gluing system for inprocess treatment of most wood-based composites.

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The present invention further provides a composition for the protection of glued wood-based products against attack and destruction of microorganisms. Such composition contains triadimefon and/or triadimenol and a glue or glue system. The preferred glues or glue systems are those mentioned above. The composition of the present invention may contain further additives such as solvents, which are compatible with the glue or glue system. The composition can alternatively be suspended in water such that the water becomes a component of the composition. The composition of the present invention can be prepared by commonly known methods, for example by mixing the single components. The composition can be used

according to the method of the present invention by addition to the wood particles during the manufacturing process of wood-based glued products.

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#### CLAIMS:

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- 1. Method of using triadimefon and/or triadimenol as a preservative for the protection of glued wood-based products against attack and destruction of microorganisms characterized in that triadimefon and/or triadimenol is applied during the manufacturing process of the glued wood-based products.
- 2. Method according to Claim 1, characterized in that the wood-based products are selected from wood fibre, wood chip or flake and thin wood veneer, plywood, laminated veneer lumber (LVL), medium density fibreboard (MDF), waferboard/strandboard/oriented strandboard (OSB) and particleboard.
  - 3. Method according to at least one of Claims 1 or 2, characterized in that triadimefon and/or triadimenol are added to the glue during the manufacturing of the woodbased products.
  - 4. Method according to at least one of Claims 1 to 3, characterized in that a mixture of glue, triadimefon

and/or triadimenol and optionally one or more solvents are applied by glue-line addition.

- 5. Method according to at least one of Claims 1 to 4,

  5 characterized in that a mixture of triadimefon and/or

  triadimenol and at least one furter active selected from

  the series of fungicides and insecticides is employed.
- 6. Method according to at least one of Claims 1 to 5, 10 characterized in that a mixture of triadimefon and/or triadimenol and at least one compound selected from tebuconazole and cyproconazole is employed.
- 7. Composition for the protection of glued wood-based
  15 products against attack and destruction of microorganisms
  containing a glue, triadimefon and/or triadimenol.
- Composition according to Claim 7, containing one or more further actives selected from fungicides and insecticides
   and optionally one or more solvents compatible with the glue or is suspended or emulsified in water
  - Composition according to Claim 7, containing water as the solvent.

10. Glued wood-based product containing triadimefon and/or triadimenol.

# INTERNATIONAL SEARCH REPORT

International application No.

PCT/NZ2003/000280

<b>A.</b>	CLASSIFICATION OF SUBJECT MATTER								
Int. Cl. 7:	B27K 3/40, 3/50, 3/38, 3/34								
According to	International Patent Classification (IPC) or to bot	h national classification and IPC							
В.	FIELDS SEARCHED								
Minimum doca B27K	umentation searched (classification system followed by	classification symbols)							
NONE		stent that such documents are included in the fields search	hed						
Blectronic data DWPI: B27	a base consulted during the international search (name of KAND TRIADIME+, B27K 3/50 AND TRI	of data base and, where practicable, search terms used) AZOL+							
C.	DOCUMENTS CONSIDERED TO BE RELEVAN	Т							
Category*	Category* Citation of document, with indication, where appropriate, of the relevant passages								
A	DE 19648888 A1 (Remmers Bauchemie G Abstract								
A	EP 533016 A1 (Bayer AG) 24 March 1993 Abstract								
A	WO 2000/71314 (Lonza Inc) 30 November 2000 Abstract								
F	Further documents are listed in the continuation	on of Box C X See patent family ann	ex						
"A" docum	is not considered to be of particular	later document published after the international filing da and not in conflict with the application but cited to unde or theory underlying the invention	ate or priority date						
"E" earlier after th	earlier application or patent but published on or after the international filing date  "X" document of particular relevance; the claimed invention cannot considered novel or cannot be considered to involve an invention								
claim(s publica	when the document is taken alone cument which may throw doubts on priority tim(s) or which is cited to establish the blication date of another citation or other special ason (as specified) when the document is taken alone document of particular relevance; the claimed invention or considered to involve an inventive step when the document with one or more other such documents, such combination a person skilled in the art								
"O" docum exhibit "P" docum	· ·	document member of the same patent family							
	ual completion of the international search	Date of mailing of the international search report 2 7 FEB 2004							
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#### INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.

PCT/NZ2003/000280

This Annex lists the known "A" publication level patent family members relating to the patent documents cited in the above-mentioned international search report. The Australian Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

	t Document Cited in Search Report			Pate	ent Family Member		
DE	19648888		NONE	·		· · · · · · · · · · · · · · · · · · ·	
EP	533016	AT	129384	CA	2078412	DE	4131184
		FI	924165	JР	5194117	NO	923330
wo	2000/71314	AU	54438/00	CA	2374884	EP	1185402
		JР	2003500374	US	6527981		
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